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Vibrational spectra and normal coordinate analysis of N-methylthiopropionamide

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Abstract : The Raman spectrum of N-methylthiopropionamide was recorded in the region 100–4000 cm^{-1}. The infrared spectra of N-methylthiopropionamide and N-deuterated N-methylthiopropionamide and their solutions in chloroform were also recorded in the range 4000–180 cm^{-1}. Normal coordinate treatment of both N-methylthiopropionamide and N-deuterated N-methylthiopropionamide was carried out using general quadratic valence force field and the force constants were refined by the damped least squares method. The potential energy distributions in symmetry coordinates are discussed in relation to the mixing of skeletal frequencies for N-methylthiopropionamide and the nature of absorption band is investigated.

Vibrational spectroscopy has proved to be of much help in elucidating the structure of amides. Infrared and Raman spectra studies of dichroism, band contour studies and normal coordinate analysis of simple primary, secondary and tertiary amides and thioamides and of their deuterated species enabled various workers to assign the skeletal frequencies and to investigate the nature of amide I, amide II and the amide III absorption bands.

In this context, the vibrational spectra of N-methylthiopropionamide have been the object of much interest. IR and Raman spectra with tentative assignments were reported by Venkata Ramiah and Usha Bai [1]. However, the IR data was limited to 400 cm^{-1}, and Raman spectrum was limited between 200–1600 cm^{-1}. The normal coordinate treatment of N-methylthiopropionamide was carried out by Raman Rao *et al* [2], but there is no report on the out-of-plane vibrations of both N-methylthiopropionamide and N-deuterated N-methylthiopropionamide.

Keywords : Vibrational spectra, N-methylthiopropionamide, N-deuterated thiopropionamide, vibrational assignment

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As there are several discrepancies in the assignments proposed in the above investigations [1,2], an attempt has been made to reinvestigate the Raman and infrared spectra by including both in-plane and out-of-plane vibrations. In the present work, we report a complete infrared and Raman data along with the results of normal coordinate analysis taking into account the internal modes of the CH_3 and CH_2 groups.

Table 1. Vibrational assignments of N-methylthiopropionamide and N-deuterated N- methylthiopropionamide.*

Species	Observed frequency			Vibrational assignments NMTP, deuterated NMTP	PED% NMTP, deuterated NMTP
	Infrared frequency and intensity NMTP cm^{-1}	Infrared frequency for deuterated NMTP cm^{-1}	Laser Raman frequency and intensity NMTP cm^{-1}		
A′	3225 S	2380 MS	3240 VS	νN–H, νN–D	$98S_1, 97S_1$
A′	2975 S	2970 MS	2980 VS	$vasy\ (C'H_3)$, $vas(C''' - H_3)$	$99S_2, 99S_2$
A′	2925 MS	2930 MS	–	vasy ($C'H_3$), vas ($C'–H_3$)	$97S_3, 93S_3$
A′	2873 VW	2865 VW	–	vsy($C''H_3$), vsy($C''' - H_3$)	$99S_4, 95S_5$
A′	2870 VW	2861 W	–	vsy($C'H_3$), vsy($C'–H_3$)	$98S_5, 98S_6$
A′	2870 VW	2860 W	–	$C''\ \begin{pmatrix} H \\ H \end{pmatrix}$ sym. stretch $C''\ \begin{pmatrix} H \\ H \end{pmatrix}$ sym. str.	$99S_6, 98S_6$
A′	1560 VS	1530 VS	1550 W	C–N stretch, C–N stretch	$44S_7, 18S_3, 20S_{11}, 16S_{23}, 68S_7, 21S_{11}, 18S_{23}$
A′	1435 MS	1435 W	1412 M	$C'''H_3$ asym. deform, $C'''H_3$ asym. deform	$72S_8, 10S_{10}, 81S_8, 12S_{10}$
A′	1430 VS	1427 VS	–	$C'H_3$ asym. deform, $C'H_3$ asym. deform	$51S_9, 28S_{14}, 62S_9, 20S_{14}$
A′	1432 MS	1421 MS	–	$C''\ \begin{pmatrix} H \\ H \end{pmatrix}$ bending, $C''\ \begin{pmatrix} H \\ H \end{pmatrix}$ bending	$21S_{11}, 15S_8, 40S_{10}, 31S_{11}, 14S_8, 52S_{10}$
A′	1365 W	1360 VW	1377 W	$C'''H_3$ sym. deform, $C''H_3$ sym. deform	$68S_{11}, 15S_{10}, 65S_{11}, 21S_{10}$
A′	1359 MS	1370 MS	1350 W	$C'H_3$ sym. deform, $C'H_3$ sym. deform	$48S_{14}, 31S_9, 51S_{14}, 31S_9$
A′	1240 S	1230 MS	1250 M	N–H deformation, N–D deformation	$32S_{12}, 34S_{17}, 38S_{12}, 30S_{17}$
A′	1204 MS	1180 VW	–	$C'''H_3$ rocking, $C'''H_3$ rocking	$68S_{15}, 21_{S2}, 61S_{15}, 20S_2$

Table 1. (*Contd.*)

Species	Observed frequency			Vibrational assignments NMTP, deuterated NMTP	PED% NMTP, deuterated NMTP
	Infrared frequency and intensity NMTP cm^{-1}	Infrared frequency for deuterated NMTP cm^{-1}	Laser Raman frequency and intensity NMTP cm^{-1}		
A'	1106 MS	1090 W	1080 M	$C'H_3$ rocking, $C'H_3$ rocking	$40S_{13}, 20S_{17}, 38S_{13}, 22S_{17}$
A'	1003 VS	1000 W	–	$C''\begin{pmatrix}H\\H\end{pmatrix}$ wagging, $C''\begin{pmatrix}H\\H\end{pmatrix}$ wagging	$42S_{16}, 21S_{19}, 42S_{16}, 28S_{19}$
A'	952 MS	928 VS	–	C–C″ stretch, C–C″ stretch	$51S_{17}, 11S_{13}, 58S_{17}, 10S_{13}, 10S_{20}$
A'	–	860 VW	905 W	N–C‴ stretch, C‴–N stretch	$49S_{18}, 21S_{17}, 61S_{18}, 11S_{17}$
A'	790 VW	790 VW	775 W	C′–C″ stretch, C′–C″ stretch	$58S_{19}, 20S_{17}, 56S_{19}, 21S_{17}$
A'	680 MS	671 VW	675 VS	C=S stretch, C=S stretch	$38S_{20}, 11S_{24}, 45S_{20}, 15S_{27}$
A'	530 VW	529 VW	–	S=C–N deform, S=C–N deform	$26S_{21}, 17S_{17}, 18S_{18}, 24S_{24}$, $32S_{21}, 18S_{17}, 20S_{18}, 21S_{24}$
A'	480 VW	470 W	480 M	C′–C″–C deform, C′–C″–C deform	$22S_{22}, 10S_{19}, 26S_{13}, 28S_{22}$, $15S_{17}, 21S_{13}$
A'	380 VW	360 VW	380 M	C – C″ rock, C – C″ rock	$32S_{23}, 15S_{19}, 38S_{23}, 21S_{19}$
A'	280 M	260 W	275 M	N – C‴ rock, N – C‴ rock	$48S_{24}, 12S_{21}, 41S_{24}, 20S_{21}$
A''	2905 MS	2873 W	–	$\nu_{asy}(CH_3)_2$, $\nu_{as}(CH_3)_2$	$97\,\nu_{as}(CH_3)_2, 95\,\nu_{as}(CH_3)_2$
A''	2990 S	2867 W	–	$\nu_{asy}(CH_3)_2$, $\nu_{as}(CH_3)_2$	$95\,\nu_{asy}(CH_3)_2, 97\,\nu_{as}(CH_3)_2$
A''	–	2855 MS	2810 VS	$\nu_{asy}(CH_2)$, $\nu_{as}(CH_2)$	$99\,\nu_{asy}(CH_2), 91\,\nu_{as}(CH_2)$
A''	1415 W	1390 W	1415 M	$\delta_{asy}(CH_3)_2$, $\delta_{asy}(CH_3)_2$	$68\,\delta_{asy}(CH_3)_2 + 21\,\gamma(CH_3)_2$ $71\,\delta_{asy}(CH_3)_2 + 18\,\gamma(CH_3)_2$
A''	1413 W	1389 VW	–	$\delta_{asy}(CH_3)_2$, $\delta_{asy}(CH_3)_2$	$64\,\delta_{asy}(CH_3)_2 + 17\,\gamma(CH_3)_2$ $67\,\delta_{as}(CH_3)_2 + 21\,\gamma(CH_3)_2$

Table 1. (*Contd.*)

Species	Observed frequency			Vibrational assignments NMTP, deuterated NMTP	PED% NMTP, deuterated NMTP
	Infrared frequency and intensity NMTP cm^{-1}	Infrared frequency for deuterated NMTP cm^{-1}	Laser Raman frequency and intensity NMTP cm^{-1}		
A″	1410 W	1387 VW	1410 M	$\delta_{asy}(CH_2)$, $\delta_{asy}(CH_2)$	72 $\delta_{asy}(CH_3)_2$ + 15 $\gamma(CH_2)$ 18 $\gamma(CH_2)$ + 69 $\delta as(CH_2)$
A″	1165 W	1150 W	–	$\gamma(CH_3)_2$, $\gamma(CH_3)_2$	54 $\gamma(CH_3)_2$ + 22 $\delta asy(CH_3)_2$, 69 $\gamma(CH_3)_2$ + 10 $\delta as(CH_2)$
A″	1150 W	1149 VW	–	$\gamma(CH_3)_2$, $\gamma(CH_3)_2$	54 $\gamma(CH_3)_2$ + 22 $\delta asy(CH_3)_2$, 55 $\gamma(CH_3)_2$ + 25 $\delta as(CH_2)$
A″	1145 W	1119 W	1140 MS	$\gamma(CH_2)$, $\gamma(CH_2)$	71 $\gamma(CH_2)$ + 26 $\delta asy(CH_2)$ 75 $\gamma(CH_2)$ + 11 $\delta as(CH_3)_2$
A″	985 W	980 W	975 M	$\omega(CH_3)_2$, $\omega(CH_3)_2$	59 $\omega(CH_3)_2$ + 10 $\tau(CH_3)_2$ 60 $\omega(CH_3)_2$ + 12 $\tau(CH_3)_2$
A″	–	979 VW	990 W	$\omega(CH_3)_2$, $\omega(CH_3)_2$	51 $\omega(CH_3)_2$ + 15 $\tau(CH_3)_2$ 51 $\omega(CH_3)_2$ + 18 $\tau(CH_3)_2$
A″	970 M	970 W	–	$\omega(CH_2)$, $\omega(CH_2)$	49 $\omega(CH_2)$ + 21 $\tau(CH_2)$, 54 $\omega(CH_2)$ + 15 $\tau(CH_2)$
A″	223 M	–	225 W	$\tau(CH_3)_2$, $\tau(CH_3)_2$	54 $\tau(CH_3)_2$ + 29 $\omega(CH_3)_2$, 49 $\tau(CH_3)_2$ + 22 $\omega(CH_3)_2$
A″	188 W	188 W	190 M	$\tau(CH_3)_2$, $\tau(CH_3)_2$	48 $\tau(CH_3)$ + 19 $\omega(CH_3)_2$, 41 $\tau(CH_3)_2$ + 18 $\omega(CH_3)_2$
A″	–	180 W	140 W	$\tau(CH_2)$, $\tau(CH_2)$	42 $\tau(CH_2)$ + 24 $\omega(CH_2)$, 52 $\tau(CH_2)$ + 26 $\omega(CH_2)$

ν – Stretch δ – deformation β – bending γ–rocking ω – wagging τ – torsion

* The symmetry coordinates (S) are available from the authors.

Pure chemicals of N-methylthiopropionamide (NMTP) obtained from Bharathidasan University was used as such without further purification, to record Raman and infrared spectra. The laser Raman spectrum of NMTP was recorded using 488 nm line of Ar^+ for excitation in the region 100–4000 cm^{-1} in Cary Model grating spectrophotometer with a 4 W Ar^+ laser. The infrared spectrum of NMTP and N-deuterated NMTP and their solutions in chloroform were recorded using Perkin Elmer 983G double beam grating spectrophotometer. N-deuteration was achieved by repeated exchanges with D_2O. The removal of D_2O was carried out at room temperature in order to minimize a possible sample deterioration which was reported in literature [3]. Experiments carried out under the same conditions used for the deuterium exchange, but using normal water as solvent, did not reveal detectable sample changes.

In order to ascertain the amount of mixing among the normal modes and to obtain a more accurate description of the fundamental vibrations of NMTP and N-deuterated NMTP, a normal coordinate analysis was undertaken. The calculations were performed using Wilson's FG matrix method with the computer programs developed by Schachtschneider [4].

The molecular skeleton is planar to a good approximation and therefore a C_s symmetry can be assumed. This results in 39 fundamental vibrations which span the irreducible representations as $24A'$ (in-plane) and $15A''$ (out-of-plane) vibrations. All the fundamental modes are active in both Raman and infrared spectra. The bond lengths used in the present investigation are C–N = 1.36 Å; C = S = 1.71 Å; N–C = 1.47 Å; C–C = 1.54 Å; C–H = 1.09 Å and N–H = 1.02 Å. These values are taken from similar related system in reference to the title molecule.

The observed and calculated frequencies, potential energy distributions (PED) in symmetry coordinates for NMTP and N-deuterated NMTP are shown in Table 1. PED in symmetry coordinates is obtained by using the formula $F_{ii}L_{ik}^2 / \lambda_k$. PED contributions below 10% are not shown in the table.

References

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